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Investigation of the continuous flow sorption of

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40heavy metals in a biomass-packed column: revisiting the Thomas design model for correlation of binary component systems†

Felycia

14E. Soetaredjo,* Alfin Kurniawan, L. K. Ong, Dimas R. Widagdyo and Suryadi Ismadji

Remediation of aquatic environments polluted by toxic heavy metals has become a focus of interest for many chemical and environmental engineers throughout the world. In the present study, rice straw was employed

32as a low-cost agricultural waste material for the removal of Cd (II) and Pb(II) ions from single and binary solutions.

Isothermal biosorption experiments were conducted at 303.15 K using a column at various flow rates and bed heights. The

3breakthrough curves for single metal systems were fitted with the Thomas,

Yoon-Nelson,

33bed-depth-service-time (BDST) and dose-response models. A new semi-empirical model based on the

classical Thomas equation has been developed for simulation of the breakthrough curves for binary metal systems. This modified Thomas model, combined with sorption- inhibiting coefficients determining competitive sorption behavior, was found to represent the Received 30th June 2014 breakthrough data very adequately. The exhausted biosorbent bed was readily regenerated using an acid Accepted 7th October 2014 elution method involving a 0.05 mol l HCl solution, and was reused for five consecutive sorption– 1 DOI: 10.1039/c4ra06425a regeneration cycles without significant loss of adsorption capacity. The used biosorbent also showed economic promise in the packed bed treatment of actual electroplating wastewater containing Cd(II) and www.rsc.org/advances Pb(II) ions. 1. Introduction With industrialization and the rapid growth of urban pop- ulations, the reserves and

15quality of surface waters are wors- ening due to excessive discharge of

pollutants into the water bodies. Among the

15various types of water pollutants, heavy metals are the most life-threatening, due to their toxicity, car- cinogenicity, resistance to biological degradation and long-term accumulation in the food chain.

1 Cadmium and lead are two heavy metals that have a number of desirable properties in a variety of industrial applications, including batteries, ammu- nition, electronic goods, metal ?nishing, and weighting and shielding applications. On the other hand, according to the priority

49**list of hazardous substances issued by the US Agency for Toxic Substances and Disease Registry** (ATSDR), **lead**

and cadmium rank second and seventh, respectively, in terms of frequency of occurrence, toxicity level and potential for human exposure.2 The removal of these heavy metals is therefore

20**a Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114,** East Java, **Indonesia. E-mail: felyciae@yahoo.com; Fax: +62 31 389 1267; Tel: +62 31 389 1264**

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra06425a matter of priority, not only in terms of environmental awareness but also for the protection of water resources. Over the past decade, adsorption has become the method of choice for the puri?cation of water and wastewater. The key advantages of adsorption methods include their high efficiency, cost-effectiveness and wide adaptability, and also the fact that they are environmentally acceptable and capable of generating effluents of high quality. The success of adsorption processes is, however, strongly dependent on selection of the adsorbent material and design of the separation unit. A wide range of materials have been evaluated for the adsorption of heavy metals, including microbial and seaweed biomass (living or dead), cellular products, activated carbons, sewage sludges, clays and clay-like minerals, hybrid materials and ordered mesoporous silica.3–12 Among these, living or dead ligno- cellulosic biomass consisting of natural polymeric materials are promising alternatives to commercial adsorbents for the puri?cation of metal-bearing effluents. These naturally occur- ring polymeric materials (e.g., lignin, cellulose and hemi- cellulose) contain hydroxyl, carboxyl, phosphate and amino functional groups, all of which possess a speci?c ability to bind heavy metals.13–15 With this in mind, rice straw residues, of which about 40 million tons per annum are generated in Indonesia alone, have been highlighted in the present study as a cheap source of biomass for the potential detoxi?cation of heavy metals in aqueous solution. In practical applications the adsorption operation is usually performed in a packed bed system, in which the effluent stream is passed through a column packed with a speci?c quantity of a suitable adsorbent. The design of a reliable packed bed adsorber requires the construction of a satisfactory modeling framework centered on establishing the shape of the break- through curve.16 The characteristic

47**shape of the breakthrough** curve **of** an **adsorption**

system depends strongly on the design data, such as ?ow rate, initial solute concentration and the dimensions of the adsorber. In recent years an increasing number of publications have appeared in the literature dealing with heavy metal adsorption in packed bed operations and breakthrough modeling.17–21 However, studies related to single- solute adsorption are not entirely relevant to practical industrial wastewater treatment. In practical wastewater treatment, two or more heavy metal species may coexist within the liquid system. Although a large number of studies have sought to establish mathematical models for simulating the breakthrough curves for binary or multicom- ponent systems, there remains a major challenge to construct a simple yet reliable model that has high accuracy and is compu- tationally efficient. The building block of most breakthrough models for heavy metal sorption is based on rate-controlling mechanisms, typical examples being ?lm diffusion, surface diffusion, pore diffusion, and combinations of these.22–24 Most, if not all, of these mass transfer-based models have had only limited success due to the complexity of the modeling, which o?en requires advanced computer resources for resolution. On the other hand a semi-empirical modi?cation of the well- established column model can be a more effective approach for constructing breakthrough curves which give a closer match to the experimental data. In line with this, the present study has aimed at providing a new column model based on the classical Thomas model, for simulation of the breakthrough curves of heavy metal (e.g., Cd

21(II) and Pb(II)) sorption from binary mixtures. The

effect of bed height and ?ow rate on the breakthrough characteristics for single and binary metal systems are discussed in detail. The practical application of rice straw in handling practical electroplating wastewater containing multiple metal ions has also been evaluated in terms of its adsorption perfor- mance and cycling efficiency, along with the possibility of transforming waste biosorbent into value-added products. 2. Experimental 2.1 Chemicals Analytical grade cadmium nitrate tetrahydrate (98%) and lead nitrate (99%) were

57purchased from Sigma-Aldrich, Singapore, and used as

supplied. Deionized water was employed throughout. 2.2 Preparation of biosorbent Rice straw was collected from a rice ?eld located in Blitar district, East Java. A?er collection the biomass was cut into pieces 1 1 cm and boiled in deionized water (solid–water ratio 1 : 10, in three successive 3 h stages) to remove colored mate- rials and water-soluble compounds. The residual solid was ?ltered off under vacuum, and washed and dried in a forced convection oven at 80 C for 48 h. The dried biomass was crushed using an IKA-Labortechnick grinder and sieved through US standard test sieve no. 50/60 (250–297 mm). The

57?nal product was stored in airtight plastic bags.

2.3 Packed-bed biosorption experiments Cadmium and lead

10solutions were prepared by dissolving a speci?c amount of the nitrate salt in 1 l deionized water to give

41an initial concentration of 0.01 mmol l 1.

Laboratory-scale

14experiments were conducted in a glass column (i.d. 3 cm, length 40 cm)

with a 0.2 cm layer of sintered discs (Por. 2 grade; United Scienti?c Industries) located at the top and bottom of the column to ensure a closely packed arrangement and prevent any loss of biosorbent. A programmable Master?ex L/S peri- staltic pump (Cole-Parmer Instrument Co.) was used to main- tain a constant ?ow rate. The experimental set-up is shown in ESI Fig. S1.† A given

42quantity of biosorbent was tightly packed into the column to give a bed height of

10, 15 or 20 cm. Precautions were taken to avoid channeling and air pockets within the packed bed by soaking the column in deionized water for 2 h before the biosorption experiments. Cd(NO3)2 or Pb(NO3)2, or an equi- molar mixture of the two, were continuously pumped

22to the top of the column (down?ow mode) at a prescribed ?ow rate

(10, 20 or 30 ml min 1). A solution of 0.1 N HCl was used to adjust the pH of the metal effluents to between 5.5 and 6.0. The column experiments were conducted at room temperature over 8 h. Preliminary

investigation showed that the bed exhaustion time (te) was 8 h (te is the time at which solute concentration in the outlet stream reaches 95% of its initial concentration). Effluent samples

16**from the exit of the column** were collected periodically **and analyzed for** residual ion **concentration.** In **the**

initial period of the experiments (2 h), 5 ml aliquots were collected every 15 min, and therea?er every half hour. Duplicate runs were conducted, and the data recorded are the mean of the two. 2.4 Determination of the residual concentration of metal ions The residual

24**concentrations of Cd(II) and Pb(II)** ions **in the** outlet stream **were**

analyzed on a Shimadzu AA-6200 atomic absorp- tion ?ame emission spectrophotometer in an air-acetylene ?ame. The calibration curves for each metal were constructed by diluting standard solutions of Cd(NO3)2 and Pb(NO3)2 (Fisher Scienti?c) to obtain working solutions of varying concentrations (0.001 to 0.01 mmol l 1). Maximum absorbance occurred at wavelength 217.0 nm for Pb(II) and 228.8 nm for Cd(II). 2.5 Characterization of biosorbent The surface topography was determined

56**on a JEOL JSM-** 6300F ?eld emission **scanning electron microscope (SEM) at an accelerating voltage of 20 kV.**

An energy-dispersive X-ray (EDX) detection system was connected to the SEM for elemental analysis. Nitrogen adsorption isotherms were measured at 77 K using a Micromeritics ASAP 2010 automated sorptometer. The

12**speci?c surface area was determined by** the **standard**

12**BET method applied to** an **adsorption** branch in the **relative** pressure **(p/p**) range **0.05–0.30. Total pore volume** (VT) **was estimated from the** quantity **of** nitrogen **adsorbed at a relative pressure of 0.99. The**

determination of metal content

10**was conducted on a PANalytical MiniPal QC energy-dispersive X-ray** ? uorescence **(EDXRF) spectrometer.**

The surface functional groups were identi?ed by infrared spectroscopy on

10**a Shimadzu FTIR 8400S spectrophotometer.** 2.6 Calculation **The**

amounts of metal ions adsorbed onto the packed bio- sorbent, also described as the dynamic uptake capacity (mmol g 1), were calculated by eqn (1): qbed ¼ Mr m ; . (1) where m is the mass of packed biosorbent (g) and Mr represents the difference (mmol) between the in?uent metal load and that leaving the column. The parameter Mr can be determined by eqn (2):25 Mr ¼ VeC0 X ðVnþ1 VnÞðCnþ1 CnÞ 2 ; (2) where Ve

5**is the throughput volume at** column exhaustion **(l),**

C0 is the in?uent metal ion concentration (mmol l 1), Vn

5is the throughput volume at the nth reading (l), Vn +1 is the throughput volume at the (n + 1)th reading (l), Cn is the outlet metal ion concentration at the nth reading (mmol l 1) and Cn +1 is the outlet metal ion concentration at the (n + 1)th reading (mmol l 1).

The quantity of metal ions in the adsorbed phase at 1% breakthrough, qb (mmol g 1), is provided by the following relationship:26 qb ¼ 100t01% mC0 ; Q (3) where t1% is the column service time (min) when the outlet solute concentration is equivalent to 1% of the inlet concen- tration,

37Q is the ?ow rate (ml min 1) and m is the mass of packed biosorbent (g).

3. Results and discussion 3.1 Characteristics of biosorbent The electron micrographs illustrated in ESI Fig. S2(a)–(c)† show a rod-like structure, the biosorbent exhibiting the smooth uniform surface of native rice straw. The EDX spectrum shown in Fig. S2(d)† con?rmed that silica and the alkali and alkaline earth metals (e.g., Na, K and Ca) were the elemental constituents of native rice straw. The presence of cadmium and lead metals was also detected in the EDX spectrum of metal-loaded rice straw (Fig. S2(e)†), con?rming that these metals were adsorbed on the surface of the biosorbent. SEM images also revealed that there had been no signi?cant structural changes between native and metal-loaded rice straw. The BET speci?c surface area of native rice straw was relatively low (39.6 m2 g 1), with a total pore volume of 0.012 cm3 g 1, supporting the SEM information that the biosorbent had a non-porous structure. The FTIR transmittance spectra (not shown) displayed a number of representative bands in native rice straw: stretching of H-bonded OH groups at 3418 cm 1, symmetrical stretching of sp3 C–H in CH2 groups near 2850 cm 1, stretching of C]O at 1758 cm 1, assigned to carboxylic acids or aliphatic esters in lignin or hemicellulose, stretching of C]C in the aromatic rings of bound lignin at 1520 cm 1, symmetrical sp3 C

50–H bending at 1361 cm 1, stretching of C–O

corresponding to glycosidic linkages in cellulose and hemicellulose near 1100

50cm 1, out-of-plane sp2 C–H bending at

675 cm 1 and Si–O–Si stretching in silica at 524 cm 1. The binding of

17Cd(II) and Pb(II) on the surface of the

biosorbent was con?rmed by the absorp- tion bands within the range 510–450 cm 1, possibly arising from the stretching vibration of M–O bonding, where M refers to the divalent Cd(II) and Pb(II) cations. Speci?cally, the coor- dination modes of metal–carboxylate complexes can be cate- gorized into unidentate coordination, bidentate chelating coordination or bidentate bridging coordination.27 Taking into account the spectral information of Dv(COO)complex and

32the possibility of interaction between divalent metal atom and the

second carboxylate oxygen of the COO moiety present in cellulose and hemicellulose structures, it can be suggested that Cd(II)– or Pb(II)–carboxylate complexes are coordinated in the bidentate bridging form. In this case, the bidentate carboxylate- binding mode is preferred to the monodentate mode, in order to minimize the steric repulsion between the incoming metal ions and the ligand moiety. Furthermore, the clear

shi? to lower wavenumbers in the position of the stretching peaks of hydroxyl and carboxylic groups near 3400 and 1750 cm 1 identi?es the chemical interaction between metal species and these surface functional groups during the biosorption process. 3.2 Breakthrough analysis

> 113.2.1 Effect of bed height. The effect of biosorbent dosage on the dynamic uptake capacity was systematically examined

by varying the bed height at constant ?ow and an initial metal ion concentration of 0.01 mmol l 1. In the present study, the performance of a packed bed was determined over relative concentrations (Ct/C0) between 0.01 (1% breakthrough) and 0.95 (95% breakthrough), derived from the safe water quality standards determined by local government.

> 33In Fig. 1 it may be seen that the gradient of the breakthrough curves

became less sharp with increasing bed height, repre- senting a greater degree of bed uptake capacity. The

> 54mass transfer zone (MTZ) (i.e., the active part of the packed bed where adsorption actually takes place) in the

Cd(II)-loaded column was 7.67, 10.47 and 11.96 cm for 10, 15 and 20 cm bed height, respectively. A longer time to reach the break point was also accomplished using beds of increased height. The dynamic uptake capacity at 1% breakthrough for a 15 cm packing height was 6.20 10 4 mmol g 1 (0.070

> 7mg g 1) for Cd and

6.72 Fig. 1 Experimental

> 38breakthrough curves for single biosorption of Cd (II) and Pb (II) ions at

various

> 16flow rates and bed heights (10 cm – 15

cm – 20 cm) and the prediction results using the

> 16Thomas, Yoon-Nelson and dose-response models.

10 4

> 9mmol g 1 (0.139 mg g 1)

for Pb; these values were increased to 6.74 10 4

> 9mmol g 1 (0.076 mg g 1)

and 7.30 10 4

9**mmol g 1** (0.151 **mg g 1),**

respectively, for a 20 cm bed height by feeding the effluent at 10 ml min 1. This indicates that an increased bed height provided a greater depth of MTZ for the metal effluent to travel before reaching the exit, thus allowing a delayed breakthrough and

53**an increase in the** throughput **volume of** solution **treated,** ulti- mately extending **the**

lifetime of the bed. With regard to bed exhaustion, beds with smaller heights become saturated more quickly due to a reduction in the number of super?cial areas of the adsorbent, and consequently the active sites available for sorption.

38**3.2.2** Effect **of** solution ?ow **rate. The breakthrough curves** for single biosorption **of** Cd **(II) and** Pb **(II)**

ions at various ?ow rates are shown in Fig. 1. An increase in steepness of the breakthrough curves was observed at higher ?ow rate, demon- strating an early breakthrough time and reduced bed exhaus- tion time. For a 20 cm bed height, as the solution ?ow

51**rate was** increased **from** 10 **to** 20 **ml min 1 for** Pb **(II)**

sorption, the breakthrough time was reduced from 171 to 73 min and the exhaustion time from 395 to 300 min. These results can be explained by considering the limited

53**contact time the** metal **effluent** makes **with the biosorbent** bed, and also **the**

limitation in the diffusion of metal ions from the liquid to the solid phase at higher ?ow rates, thus reducing the volume of solution being treated and consequently decreasing the dynamic uptake capacity of the bed. Furthermore, lower adsorption capacity at 1% breakthrough was obtained at higher ?ow rates. For example, by doubling the ?ow rate from 10 to 20 ml min 1, the 20 cm breakthrough capacity of Cd(II) decreased from 6.74 10 4

9**mmol g 1** (0.076 **mg g 1)**

to 5.72 10 4

9**mmol g 1** (0.064 **mg g 1),**

and a further decrease to 4.48 10 4

9**mmol g 1** (0.050 **mg g 1)**

was noted

26**as the** ?ow **rate increased to** 30 **ml min 1.**

3.3 Breakthrough modeling for the biosorption of single metals The

> 3**design and optimization of the breakthrough curve for a full-scale column** adsorption **system requires a simple modeling approach that can provide accurate scale-up column data. In the present study, the Thomas,** Yoon-Nelson, BDST **and**

dose-response empirical models

> 3**were employed to analyze the breakthrough curves for single metal systems. The Thomas model is one of the** most celebrated **models** used **for**

describing column performance and the

> 14**breakthrough curve, based on** the **Langmuir adsorption–desorption isotherms** for the equilibrium **and** the **second-order reversible reaction kinetics** for **the**

rate driving force without external and interparticle diffusion limi- tations.28 The Thomas

> 37**model has the following form:** Ct **C0**

1 þ exp KTh=Q ¼ 1 ; (4) ðqmaxm C0VTÞ

> 18**where KTh is the Thomas rate constant (ml** mmol **1** min **1),** qmax **is the** intrinsic property **of**

the adsorbent representing the

> 30**maximum solid-phase concentration of solute (mmol g 1),** m **is** the mass **of adsorbent** (g), C0 is **the**

inlet concentration of solute (mmol

> 18**l 1),** Ct **is the** exit **concentration** of solute **at time t** (mmol **l 1), Q is the** solution ? ow **rate (ml min 1)** and VT is **the**

cumulative throughput volume (l) of treated solution. The determination of Thomas parameters (KTh and qmax) was con- ducted by plotting

> 22**ln(C0/Ct 1) versus** t to give **a straight line, with slope** and intercept **of** KThC0 **and**

(KThqmaxm)/Q, respectively. The second

3**model applied for correlating the breakthrough curve was the** Yoon-Nelson **model.**

This model was developed by assuming that the

19**rate of decrease in the probability of adsorption for each** solute was **proportional to the probability of** its sorption **and the breakthrough on the adsorbent.** 29 The original **and linearized** forms **of** the **Yoon-Nelson model for single component** adsorption may be **expressed**

by eqn (5) and (6), as follows: Ct expðKYNt KYNsÞ C0 1 þ expðKYNt KYNsÞ ¼ (5) ln C0Ct Ct ¼ KYNt KYNs; (6) where s is the time (min) theoretically required to achieve 50% adsorbate breakthrough and KYN is the Yoon-Nelson rate constant (min 1). The third model used for breakthrough curve analysis was the BDST model. The underlying assumption of the BDST model is

28**that the adsorption rate is proportional** both **to the** unused **capacity of the adsorbent and** to **the** remaining **concentration of** solute in **the**

liquid phase, by neglecting the axial dispersion factor. The BDST model is regarded as a simple yet reliable model based on physical measurement of the adsorption

43**capacity of the bed** for **different breakthrough values. The** classical **BDST model**

is expressed as follows:30 ln CC0b 1 ¼ lnðexpðKaN0Z uÞ 1Þ KaC0t; (7) where Cb

47**is the** desirable **breakthrough concentration (mmol l 1), Z is the bed**

height (cm), N0 is the volumetric

23**sorption capacity of the bed** (mmol **l 1), Ka** is **the** adsorption **rate constant (l** mmol min **1), and** u **is the linear velocity** 1 obtained **by dividing the** solution ?ow **rate by the** cross- sectional **area** of the bed **(cm min 1).**

Eqn (7) has been further modi?ed by Hutchins31

8**to estimate the bed** height required **for a given service time**

at breakthrough point: tb ¼ CN00u Z 1 ln C 0 Ka C0 C 1 b when expðKaN0Z=uÞ[1 (8) Solving eqn (8) for Z by substituting tb ¼ 0: Z0 ¼ N0Ka ln Cb 1 ; u C 0 (9) where Z0 is the minimum theoretical height required to give an exit concentration of Cb at zero time. Z0 is o?en referred to as the critical bed height, and is clearly equal to the mass transfer zone length (MTZL). The dose-response model, ?rst proposed by Viraraghavan and his group,32 is an empirical model describing the biosorption of heavy metals during column operation. In practice, this model is better able to describe the

30**kinetics of metal removal by the adsorption column** than **the** Bohart–Adams or **Thomas**

models, especially at lower and higher time periods on the breakthrough curve. The mathe- matical expression of the dose-response model is presented in eqn (10): C t ¼ b0 b 0 C 0 . d ; (10) 1 þ VT b1 where the parameter b0 is the expected response when satura- tion is reached, and is equal to unity as the time or throughput volume tends to in?nity. The parameter b1 indicates the throughput volume

46**at which half of the maximum response occurs**

and m is a constant for the model. The dose-response model can be expressed differently by making b0 ¼ 1: C t 1 1 . C0 ¼ d ; with b1 qm C0 ¼ (11) 1 þ VTC0 qm . The regression analysis of all column models against experimental breakthrough data was performed using Systat SigmaPlot 12.3.1 so?ware, and the correlation model parame- ters obtained were used to construct the predicted break- through curves shown in Fig. 2. The accuracy of prediction of the models

41**was further** determined **by** computing **the root mean square error (RMSE),** de? ned **as**

follows: vffiffiffi

7**bed heights** (solution **flow rate:** 10 **ml min 1** and influent **metal concentration:** 0.01 mmol **l 1)**

Thomas model Metal Bed height (cm) KTh (l

9**mmol 1 min 1)** qmax **(mmol g 1)** qbeda **(mmol g 1)**

RMSE R2 Cadmium Lead 10 3.06 15 2.71 20 2.64 10 3.25 15 2.87 20 2.79 1.62 10 3 1.39 10 3 1.20 10 3 1.79 10 3 1.54 10 3 1.32 10 3 1.39 10 3 1.18 10 3 1.09 10 3 1.53 10 3 1.29 10 3 1.18 10 3 0.056 0.046 0.029 0.089 0.025 0.016 0.948 0.976 0.981 0.940 0.972 0.984 Yoon-Nelson model s Metal Bed height (cm) KYN (min 1) (min) sexp (min) RMSE R2 Cadmium Lead 10 15 20 10 15 20 0.030 194 0.027 246 0.026 285 0.034 170 0.028 241 0.026 282 182 0.060 236 0.048 293 0.034 180 0.079 238 0.051 271 0.023 0.943 0.967 0.982 0.949 0.960 0.977 Dose-response model Metal Bed height (cm) q (mmol g 1) b1 (ml) d RMSE R2 Cadmium 10 15 20 Lead 10 15 20 a Dynamic uptake capacity, determined by eqn (1). 1.47 10 3 1.30 10 3 1.15 10 3 1.42 10 3 1.27 10 3 1.18 10 3 1721.37 3.94 2284.10 4.86 2694.45 6.42 1428.62 3.89 2231.39 4.89 2764.74 6.44 0.038 0.993 0.031 0.995 0.021 0.998 0.025 0.997 0.024 0.996 0.022 0.997 The maximum bed adsorption capacity obtained from the Thomas model prediction ranged between 0.92 10 3 and 1.79 10 3 mmol g 1 within the experimental conditions. However, the prediction overestimated the qbed values obtained from eqn (1) by between 10 and 21%. This conspicuous difference has also been observed in a number of other column studies.34–36 The increase in adsorption rate constant with ?ow rate might be attributed to a decrease in the ?uid-?lm mass transfer resis- tance, meaning that solute molecules could diffuse more easily

8**from the liquid to the solid phase. The**

correlation of column data by the Yoon-Nelson model also indicated that the time required for adsorbing 50% of the initial concentration decreased with increasing ?ow rate and decreasing bed height. In addition, the estimate of the time required to reach 50% breakthrough was very

52**close to the values obtained** experimentally. The **breakthrough curves** predicted by **the**

dose-response model showed an excellent ?t to the experimental data. The column parameters associated with this model (q, b1 and d) con?rmed the dependence of these parameters on ?ow rate and the height of packed biosorbent. With an increase in mass of biosorbent from 11.71 g (10 cm) to 23.43 g (20 cm), the values of parameter q decreased from 1.42 10 3 to 1.18 10 3 mmol g 1 for Pb(II). The adsorption capacity of Cd(II) at 50% break point increased from 1.15 10 3 to 1.82 10 3 mmol g

261 **as the** ?ow **rate increased** from 10 **to** 30 **ml min 1;**

a similar effect applied to Pb(II) sorption. The parameter b1 associated with the volumetric throughput at 50% break point also increased

25**with increasing bed height and ?ow rate. The** values **of**

q and b1 were each in conformity with the experimental data. The model constant (d)

11**increased with increase in bed height and decrease in** ?ow **rate,**

suggesting that parameter d of the dose-response model might be related to the design of the ?xed bed column, with improved adsorption performance. The relationship between bed height and breakthrough level can be studied by applying the BDST model to the column data. ESI Fig. S3† shows the speci?c trends in the BDST column parameters (N0, Ka and Z0) with variation in the breakthrough points. The dynamic bed capacity of Cd(II) gradually increased from 0.127 to 0.154 mmol l 1 within a 1–40% breakthrough range. Within a breakthrough range of 60–95%, the dynamic bed capacity decreased and then increased to its highest point, 0.160 mmol l 1. A similar trend was observed in the sorption of Pb(II), in which there was a sharp increase in the value of N0 Table 2 The correlation parameters

35**of the Thomas, Yoon-Nelson and** dose-response **models for** single **removal of** Cd **(II)**

and Pb(II) ions at varying solution flow rates (bed height: 20 cm and influent metal concentration: 0.01 mmol l 1)

34**Thomas Model** Metal **Flow rate (ml min 1) KTh** (l **mmol 1** min **1)** qmax **(mmol g 1)**

qbeda (mmol g 1) RMSE R2 Cadmium 10 20 30 Lead 10 20 30 2.64 1.20 3.15 1.03 3.36 0.92 2.79 1.32 3.24 1.22 3.45 1.11 10 3 1.09 10 3 0.85 10 3 0.79 10 3 1.18 10 3 1.08 10 3 0.96 10 3 0.029 10 3 0.022 10 3 0.052 10 3 0.016 10 3 0.024 10 3 0.023 0.981 0.958 0.965 0.984 0.941 0.958 Yoon-Nelson model Metal

7**Flow rate (ml min 1)** KYN **(min 1)** s **(min)**

sexp (min) RMSE R2 Cadmium Lead 10 20 30 10 20 30 0.026 285 0.029 168 0.033 157 0.026 282 0.030 190 0.035 139 293 0.034 147 0.074 142 0.041 271 0.023 180 0.051 128 0.051 0.982 0.954 0.968 0.977 0.948 0.939

8**Dose-response model Metal** Flow rate **(ml min 1) q** (mmol **g 1)**

b1 (ml) d RMSE R2 Cadmium 10 20 30 Lead 10 20 30 a Dynamic uptake capacity, determined by eqn (1). 1.15 10 3 1.21 10 3 1.82 10 3 1.18 10 3 1.46 10 3 1.57 10 3 2694.45 6.42 2835.03 3.89 4264.26 3.64 2764.74 6.44 3420.78 4.03 3678.51 3.62 0.021 0.998 0.022 0.998 0.032 0.995 0.022 0.997 0.030 0.995 0.023 0.998 between 1% and 40% breakthrough, followed by a slight increase over the breakthrough range 60–95%. At low break- through points,

48**there are a large number of** vacant **adsorption sites on the**

biosorbent, allowing metal ion uptake to occur with limited or no resistance. The dynamic capacity at 95% break- through (saturation) was found to be 0.160 mmol l 1 (0.11

6**mg g 1) for** Cd **(II) and 0.** 198 mmol l **1**

(0.25

6**mg g 1) for Pb(II).**

Meanwhile, a gradually diminishing rate of transfer of solute from bulk ?uid to the solid phase (Ka) with increasing break- through level was noticed, and the value of Ka remained rela- tively constant between 60

and 95% breakthrough. This might be ascribed to the limited degree of metal ion uptake, since more adsorption sites were occupied and an increasing proportion of the packed bed became saturated as the volume of effluent ?owing into the column increased. The effect of diffusional resistance might also contribute signi?cantly at high-end breakthrough levels, leading to slower uptake of metal ions. The critical bed heights calculated at various breakthrough points

7showed a trend similar to that of the adsorption rate constant. For

breakthrough points beyond 50%, it was not possible to calculate the critical bed height, due to the negative value of the natural logarithmic expression in eqn (9). This has also been con?rmed by other authors,37–39 indicating that the BDST model may be used only for interpretation of the initial part of the breakthrough curve, up to 50% breakthrough. At 50% breakthrough the natural logarithmic expression in eqn (8) is reduced to zero and the bed capacity is estimated to be 0.157 mmol l 1 (0.11

6mg g 1) for Cd (II) and 0. 194 mmol l 1

(0.24

6mg g 1) for Pb(II).

These values are considerably lower than those reported by Bhatia and his group39 for cadmium and lead ions removal in a ?xed-bed column by a macro-fungus. They obtained an estimated 50% breakthrough capacity per unit bed volume of 8.54 and 7.72 mmol l 1 for Cd(II) and Pb(II) ions, respectively. The fruit body of the oyster mushroom (Pleurotus platypus) has

5been utilized for the ?xed-bed column removal of Cd(II) from industrial wastewater

by Vimala and co-workers.40 A breakthrough capacity per unit bed volume of 21.51 mmol l 1 was obtained from the BDST model prediction. A low adsorption capacity of the biomass bed was expected, and was probably due to the initial metal concentration used in the column experiments. It is well known that

22adsorption is a concentration-driven surface phenomenon, and the depen- dence of

dynamic bed capacity on the initial solute concen- tration is con?rmed mathematically from the slope of the linear BDST plot in eqn (8). We purposely used low in?uent metal concentrations (1.12 mg l 1 of Cd(II) and 2.07 mg l 1 of Pb(II)) to represent the actual range of heavy metal contami- nation present in local public water systems. Other ?xed bed column parameters (e.g., linear velocity) and the characteristics of the packing adsorbent might also contribute to determining the bed uptake capacity. Table 3 summarizes a

27comparison of the adsorption performance of various biosorbent materials

27for the single removal of Cd(II) and Pb (II) ions

in a ?xed bed operation. The poor prediction of the BDST model beyond a 50% breakthrough point could be attributed to the complex mechanisms of the binding of metal ions by the biosorbent, which might involve two or more rate- limiting steps, including ion exchange, coordination, complexation, chelation, micro-

precipitation, adsorption and surface adsorption–complexation. Interestingly, the curve shows an S-like pattern for the variation of critical bed height with breakthrough points (ESI Fig. S3†), con?rming the inter-relationship of critical bed height and axial ?ow of MTZ inside the bed column. Based on an analysis of all the column models discussed above, it could be deduced that the Yoon-Nelson and dose- response models provided a satisfactory representation for the present column system with respect to statistical parameters (RMSE or R2) and the theoretical justi?cation of the model parameters. From the goodness-of-?t point of view, the Thomas, Yoon

26-**Nelson and dose-response models were** all **in** general acceptable. While **the**

BDST model demonstrated a satisfying linear correlation between column service time and bed height, the failure of this model beyond 50% breakthrough was inevitable. Further weaknesses of the BDST model were, ?rstly, that it assumed the adsorption of single solute in the liquid phase system and, secondly, it was unable to address the important effect of changes in pH, ionic form of the adsorbent or solute concentration on the column performance.37 Regarding the Thomas model, the prediction of column kinetic data fell reasonably within the measured range, although a fairly signi?cant deviation ten- ded to occur within the initial part of the breakthrough curves. Additionally, a packing height of 10 cm was consid- ered as the optimum bed height, since an increase in packing height of 5 cm or 10 cm to this point was insigni?cant in terms of the percentage metal removal (Table 4). 3.4 Breakthrough modeling for biosorption of binary component metals

21**In the present study, the** simultaneous biosorption **of** Cd **(II) and Pb(II)**

ions onto packed rice straw was conducted at ?ow rates of 10, 20 and 30

8**ml min 1 and** packing **heights of** 10, 15 **and** 20 **cm.** An equimolar **binary**

mixture containing 0.01 mmol l 1 of Cd(II) and Pb(II) ions was used as the effluent model. The breakthrough curves for binary metal solutions were required in order

36**to study the** effect **between the metal ions and** to assess **the adsorption**

selectivity for one metal in the presence of another in a continuous ?ow system. In this regard, a modi?ed Thomas design model incorporating the sorption-inhibiting coefficients was for the ?rst time proposed to simulate the breakthrough curves of binary metal systems. The general view of binary and/or multicomponent systems is that the solute species compete with one another for the available adsorption sites on the solid surface. Such behavior affects the rate of sorption of each solute, and consequently its concentration in the adsorbed phase. Therefore, the effect of competitive adsorption should be incorporated in the design model, and for this purpose we have introduced two dimen- sionless parameters as follows: I12 ¼ q2 q1 þ q2 and I21 ¼ q 1 q1 þ q2 ; (13) (14) Table 3 Comparison of BDST model-predicted bed capacity of various biomass materials

27**for the removal of Cd(II) and** Pb **(II) ions**

in fixed bed column operation Column parameters In?uent Concentration Predicted bed Biomass (mmol

8**l 1) Flow rate (ml min 1) Bed Height (cm)**

capacity (mmol l 1) Reference P-doped rice husk Wheat straw Allspice residue Sun?ower waste carbon calcium-alginate beads Macro fungus (Pycnoporus sanguineus) Macro fungus (Pleurotus platypus)

Filamentous green algae (Spirogyra neglecta) Spent Agaricus bisporus Palm oil boiler mill ?y ash Rice straw 0.05 –

17**Pb(II) 0.** 89 – **Cd(II) 0.** 07 – Pb **(II) 0.** 09 – Cd **(II) 0.** 7 – Cd(II) **0.** 38 – **Pb(II) 0.** 09 – **Cd(II) 0.** 24 – Pb **(II) 0.** 24 – Pb **(II) 0.** 18 – **Cd(** II) **0.** 01 – Cd **(II)**

0.01 – Pb(II) 20 10–30 1000 50–200 20 15 1 10–30 10 4–15 5 5–15 5 1 5 4 5 1–2 10 10–20 2.51 10 3 2.77 11.75 – Pb(II) 0.07 7.72 – Pb(II) 8.54 – Cd(II) 21.51 0.88 32.01 75.80 0.157 – Cd(II) 0.194 – Pb(II) 20 34 38 39 40 41 42 43 44 This study Table 4 The breakthrough parameters for single biosorption of Cd(II) and Pb(II) ions at various

58**bed heights and flow rates** Metal **Bed height (cm) Flow rate (ml min 1)** tba **(min)** tea **(min)**

MTZc (cm) qbb (10 4 mmol g 1) Ve (ml) % Rd Cadmium 10 15 20 Lead 10 15 20 10 68 20 27 30 15 10 109 20 48 30 25 10 158 20 67 30 35 10 72 20 32 30 18 10 118 20 51 30 29 10 171 20 73 30 42 292 7.67 210 8.71 205 9.27 361 10.47 240 12.00 233 13.39 393 11.96 272 15.07 267 17.38 270 7.33 212 8.49 178 8.99 361 10.10 271 12.18 210 12.93 395 11.34 300 15.13 237 16.46 5.81 2920 4.61 4200 3.84 6150 6.20 3610 5.46 4800 4.27 6990 6.74 3930 5.72 5440 4.48 8010 6.15 2700 5.47 4240 4.61 5340 6.72 3610 5.81 5420 4.95 6300 7.30 3950 6.23 6000 5.38 7110 93.5 85.6 78.7 93.8 85.8 79.2 94.0 86.1 79.4 95.4 87.6 81.2 95.7 87.8 81.5 96.1 88.2 82.0 a Experimentally determined from Fig. 1, tb and te were considered at 1% and 95% break points, respectively. b The bed adsorption capacity at 1% breakthrough, determined by eqn (3). c

31**Mass transfer zone is** calculated **by** Z ¼ **(1**

tb/te)

31**where Z is the bed height (cm).**

d Removal percentage was calculated by dividing Mr with the in?uent metal load (VeC0). where q1 and q2 represent the amounts of metal ions adsorbed, I12 and I21 are the sorption-inhibiting coefficients of component 2 (Pb(II)) to component 1 (Cd(II)) and vice versa. q1 and q2 are each treated as fractional parameters which account for the coordination complexes of metal ions with surrounding anions on the surface at the point of saturation. By introducing parameters I12 and I21 into the original Thomas model for each adsorbed component a modi?ed Thomas model was obtained, with the inclusion of competitive adsorption behavior: Ct 1 C0 ¼ 1 1 þ exp KTh;1ð1 I12Þ (15) Q q 1;max m C0;1 VT Ct C0 ¼ 1 ; (16) 2 1 þ exp KTh;2ð1 I21Þ q2;maxm C0;2VT Q where KTh,1 and KTh,2 are the sorption rate constants of component 1 and component 2 obtained from a single solute system (l mmol 1 min 1), and q1,max and q2,max are the maximum bed sorption capacity for component 1 and compo- nent 2 in the binary system (mmol g 1). q1, q2, q1,max and q2,max are ?tted parameters, whose values can be determined by linear or nonlinear regression methods. The underlying assumptions of the proposed model are: (i) that the adsorption equilibrium is nonlinear and is well represented by the Langmuir isotherm; (ii) that the rate driving force obeys second-order reversible reac- tion kinetics, (iii) there is no axial dispersion; and (iv) that the adsorption system operates isothermally under given conditions. The solution of eqn (15) and (16) can readily be obtained by nonlinear regression curve ?tting, using Systat SigmaPlot 12.3.1 so?ware or the Microso? Excel ‘Solver’ function. To start the computation the initial values of all the ?tted parameters were randomly estimated, with the following constraints: q1 > 0, q2 > 0, q1,max > 0, q2,max > 0 and q1 + q2 < 1. The computation was conducted point by point until the tolerance and convergence tests were ful?lled. We considered that the total portion of metal ions adsorbed on the surface (q1 + q2) was less than unity, by considering the free-volume fraction (porosity) in a ?xed bed in which adsorption did not take place. The bed porosity (3) was determined using eqn (17): 3 ¼1 rb=rs ; (17) where rb and rs are the tapped

11**bulk density of the packed bed**

(g ml 1) and the density of solid particles (g ml 1), respectively, experimentally determined using a density meter. The appli- cations of eqn (15) and (16) in correlating the experimental breakthrough data for an equimolar binary mixture of Cd

36**(II) and** Pb **(II)** ions **are shown in Fig.** 2, and **the values of** the ?tted **and**

calculated model parameters are summarized in Table 5. It has been shown in Fig. 2 that the modi?ed Thomas model correlated well with the experimental breakthrough curves for binary system (R2 0.99), but the graphical ?t

42**showed that the** original **Thomas model** (solid lines) **was** generally inadequate **for** describing **the**

binary adsorption breakthrough curves, and an amplifying con?rmation was provided by the coefficient of determination (0.5 < R2 < 0.7). The incorporation of the dimensionless parameters, q1 and q2, to account for the effect of competitive adsorption between two solutes was therefore helpful in improving the goodness-of-?t of the proposed model. The values of the calculated parameters (KTh,1 and KTh,2) con? rmed the applicability of the proposed modi?ed Thomas model, in which the adsorption rate constants for each solute in the binary system were lower than the corresponding values for Table 5 The fitted and calculated parameters of the modified Thomas model for binary sorption of Cd(II) and Pb(II) ions at various

7**bed heights and flow rates** Experimental **Bed height Flow rate** (cm) **(ml min 1)** qbed **,1**

qbed,2 (mmol g 1) (mmol g 1) Fitted parameters qmax,1/bin qmax,2/bin q1 q2 (mmol g 1) (mmol g 1) Calculated parameters I12 I21 KTh,1/bin (l mmol 1 min 1) KTh,2/bin (l mmol 1 min 1) RMSE R2 10 10 20 30 15 10 20 30 20 10 20 30 1.24 10 3 1.74 10 3 2.06 10 3 0.95 10 3 1.31 10 3 1.49 10 3 8.74 10 4 1.12 10 3 1.35 10 3 1.44 10 3 1.96 10 3 2.38 10 3 1.12 10 3 1.53 10 3 1.75 10 3 9.48 10 4 1.34 10 3 1.56 10 3 0.35 0.42 0.37 0.43 0.40 0.45 0.36 0.42 0.38 0.44 0.40 0.45 0.36 0.42 0.38 0.44 0.41 0.46 1.41 10 3 1.96 10 3 2.33 10 3 1.08 10 3 1.46 10 3 1.62 10 3 9.71 10 4 1.24 10 3 1.48 10 3 1.57 10 3 2.13 10 3 2.69 10 3 1.29 10 3 1.75 10 3 1.92 10 3 1.08 10 3 1.44 10 3 1.71 10 3 0.55 0.45 0.54 0.46 0.53 0.47 0.54 0.46 0.54 0.46 0.53 0.47 0.54 0.46 0.54 0.46 0.53 0.47 1.38 1.79 1.69 1.92 1.86 2.08 1.25 1.55 1.57 1.84 1.74 1.94 1.21 1.51 1.45 1.75 1.58 1.83 0.024 0.987 0.017 0.993 0.019 0.995 0.021 0.989 0.017 0.992 0.017 0.995 0.020 0.984 0.014 0.997 0.022 0.991 the single system. The presence of competing solutes not only sorption-inhibiting coefficients of the two metal ions showed a decreases the adsorption rate constant, but also the maximum weak dependence on variation in ?ow rate and bed height.

28**solid phase concentration of** each **solute. The** values **of** the According to **the**

results obtained, it can now be suggested that fractional parameters, q1 and q2, obtained by non-linear on changing either the ?ow rate or the bed height, the extent of regression analysis showed that higher amounts of Pb(II) were competition between the adsorbed components remains sorbed on the packed bed. essentially unchanged. Our hypothetical conclusion is that the EDXRF was performed to analyze the heavy metal content in extent of competition between the two solutes is more depen- the packed bed and to examine the conformity between EDXRF dent on their initial concentrations in the binary system. measurement and its theoretical calculation. The results indi- Accordingly, further systematic investigation in this direction cate an error of at most 18% between the EDXRF measurement will be necessary by conducting the sorption-column tests using and the theoretical calculation, indicating that q1 and q2 can be mixtures of various solute compositions. treated as fractional parameters representing the amount of solutes

adsorbed, in addition to the empirical correction coef- 3.5 Desorption studies and solid waste management ? cients for improving the graphical ?t.

48**The maximum** bed **adsorption capacity of Cd(II)**

predicted by the modi?ed Thomas Once the biosorbent bed has become saturated with the metal model declined from 1.62 10 3 mmol g 1 (0.18 mg g 1) to ions, it is necessary to recover the metal species to allow the bed 1.41 10 3 mmol g 1 (0.16 mg g 1) when Pb(II) was present in to be reused, and hence reduce operating costs. Column the effluent for the ?xed bed experiment at a ?ow rate of 10 ml regeneration studies were conducted over ?ve cycles of min 1 and 10 cm bed height. Under these conditions, the adsorption–desorption using hydrochloric acid at three maximum adsorption capacity of Pb(II) in the binary system was different concentrations (0.1, 0.3 and 0.5 N) as desorbent. The 1.57 10 3 mmol g 1 (0.33 mg g 1), compared to 1.79 10 3 ?ow

34**rate of the** desorbent **solution was maintained at** 10 **ml**

mmol g 1 (0.37 mg g 1) in the single system. min 1 using a peristaltic pump in the up-?ow mode. Samples Regarding the ?tted parameters, q1 and q2, it can be implied from the upstream of the column were collected every 10 min that Pb(II) ions were adsorbed in preference to Cd(II), which may for analysis. The breakthrough time (min), exhaustion time be ascribed to the

6**smaller hydrated** ionic **radius of Pb(II)**

(4.01 Å) (min) and breakthrough capacity

6**(mmol g 1)** were determined **than Cd(II)**

(4.26 Å). It has been noted that the greater the for each sorption–regeneration cycle, and the results are shown hydration of the ion, the farther it is from the adsorbing surface, in Table 6. As shown in this table, a decreased breakthrough and the weaker its adsorptive capability. A consistent link

39**time and exhaustion time was observed as the** sorption–regen- between **the**

hydrated ionic radii of the metals and their eration cycles progressed. The regeneration efficiency (%) was dynamic adsorption capacity was con?rmed in the present calculated using eqn (18): study. Furthermore, according to Pearson's hard and so? Efficiency ð%Þ¼ qR=qo 100; (18) (Lewis) acids and bases concept,45 the Cd(II) cation is a “so?” Lewis acid, whereas the Pb(II) cation is a borderline Lewis acid. where qR is the adsorption capacity of the regenerated bio- The Pb(II) cation can therefore form stronger complexes than sorbent bed at the nth cycle (mmol g 1) and qo is the original the Cd(II) cation with electronegative ligands that are “hard” adsorption capacity of the biosorbent bed (mmol g 1). Lewis bases, such as F , OH or RO (carboxylate oxygen). Fig. 3 shows a set of graphical information about the Increasing the solution ?ow rate resulted in an increased desorption pro?les of cadmium and lead ions through a 10 cm level of metal complex on the surface, whereas an increase in packed bed. A 93% recovery of Cd(II) was achieved by placing the bed height had a small or no effect. Interestingly, the calculated exhausted bed in contact with 0.1 N HCl solution for 50 min, corresponding to a throughput volume of 0.50 l. A?er 30 min, a ?ve-fold increase in the concentration of HCl solution resulted in an increase in desorption efficiency from 74.6 to 91.1%. On the other hand, 0.1 N HCl (0.60 l) gave almost complete desorption of Pb(II) ions (98%), and the throughput volume was reduced to 0.50 l using 0.5 N HCl solution. Desorption of metal ions from the biosorbent wall takes place through an equivalent exchange reaction in which one mole of divalent Cd(II) or Pb(II) ions is displaced by two moles of H+ ions.46 Thus, an increase in the concentration of H+ ions in the desorbent solution leads to an enhanced exchange perfor- mance between H+ ions and metal ions

25**at the solid–solution interface. The** stability performance **of the**

biosorbent bed for up to ?ve successive sorption–regeneration cycles was evaluated and the results are presented in Fig. 3(b). Prior to further cycles of adsorption–desorption, the eluted bed was washed a number of times with deionized

10**water, until the pH of the washing** solu- tion **was in the range**

5.0–6.0. The washing step is essential to remove excess H+ ions deposited on the surface of the bio- sorbent.

11**It was** shown **that the adsorption capacity of the bed**

was almost equal for the ?rst two cycles, but then dropped progressively from the third cycle to the ??h. The desorption of Pb(II) was nearly 90–92%, and in excess of 94% of sorbed Cd(II) was desorbed in each successive cycle. The lower desorption efficiency of Pb(II) re?ects once again the higher adsorption affinity of the biosorbent for this metal ion. Compared to the original bed sorption capacity, the values a?er the ??h cycle corresponded to 84.64% for Cd(II) and 79.50% for Pb(II), showing good adsorptive retention efficiency, even though the biosorbent bed had been reused several times. By the end of the ??h cycle, about 2.97 and 3.26 l of individual effluents con- taining Cd(II) or Pb(II) ions had effectively been treated to reach the permissible concentration prior to discharge. The loss of biosorption performance a?er the bed had been consecutively regenerated and reused was due mainly to the detrimental effect of desorbing solution.47 Continual contact between HCl solution and biosorbent bed not only resulted in the dislocation of sorbed metal ions, but led also a gradual deterioration in the biosorbent structure. The SEM image in Fig. 3(c) shows some visible changes on the biosorbent surface structure a?er multiple sorption–regenera- tion cycles, indicating the

39**leaching effect of** hydrochloric **acid during desorption,** which **may be responsible for the**

reduced metal biosorption capacity of the regenerated bed. An addi- tional plausible reason for the decrease in the bed adsorption capacity during further cycles of adsorption and desorption could be the incomplete desorption of metal ions. The management of solid waste is an environmental concern which has to be taken into account, since the disposal of metal- laden adsorbent on the land can contaminate the soil and leach into groundwater. The conversion of waste adsorbent materials to high-value end-products is therefore of considerable interest for environmental sustainability. The adsorptive capacity of the regenerated bed was considerably reduced a?er the tenth cycle, when less than 10% of its original adsorption capacity was retained. Elemental analysis by an EDXRF technique showed that the biosorbent bed contained 0.15 mmol g 1 (1.69 wt%) of Cd(II) and 0.16 mmol g 1 (3.31 wt%) of Pb(II). An effective treatment for the solid waste is to employ a two- step thermal activation process at 700 C for 4 h under a nitrogen atmosphere, followed at 900 C for 2 h in an oxidizing (air) environment, producing activated carbon of high surface area. The porous properties and structural morphology of the resultant activated carbon are given in ESI Table S1 and Fig. S4, respectively.† The cadmium oxide- and lead oxide-impregnated carbons are each high-value products and may be further applied in a composite electrode for the electrocatalytic sensing of gaseous, inorganic and organic analytes,48 catalysis of various oxidation and reduction reactions of gases and/or liquid chemicals,49 or sorption-based water puri?cation.50 3.6 Scale-up treatment of actual electroplating wastewater For the scale-up experiments, the height and internal diameter of the column were 100 and 8 cm, with a scale-up ratio of 2.50- fold and 2.67-fold, respectively, from a laboratory-scale glass column. The detailed data of the scale-up parameters are given in ESI Table S2.† Actual electroplating wastewater was collected from a metal coating and plating unit located at the Surabaya Industrial Estate, Rungkut, East Java. The Table 6 The breakthrough parameters of the original and regenerated biosorbent bed after five sorption-regeneration cyclesa Desorption Regeneration Metal Cycle no. tb (min) te (min) qbb (mg g 1) qeb

(mg g 1) (mg g 1) efficiency (%) Cadmium Lead 1 68 2 65 3 60 4 54 5 50 1 72 2 70 3 65 4 62 5 57 292 0.065 287 0.062 275 0.058 262 0.052 247 0.048 270 0.127 262 0.124 252 0.115 240 0.110 215 0.101 0.280 0.276 0.264 0.252 0.237 0.478 0.464 0.446 0.425 0.380 0.265 Original 0.263 98.57 0.251 94.29 0.242 90.00 0.227 84.64 0.439 Original 0.420 97.07 0.411 93.31 0.389 88.91 0.343 79.50 a Note: bed height: 10 cm and ?ow rate of the metal in?uent and desorbing solution (0.5 N HCl): 10 ml min 1 b . The bed adsorption capacity at 1% and 95% breakthrough were calculated using eqn (3). Fig. 3 (a) Desorption curves of Cd(II) and Pb(II) ions by HCl treatment at various concentrations; (b) the metal adsorptive retention after five sorption–regeneration cycles; and (c) SEM image shows the resulting morphology of biosorbent after desorption with 0.5 N HCl solution. characteristics of the wastewater, including pH, total dissolved solids and chemical oxygen demand were analyzed using standard methods and the average concentrations of heavy metal species were measured using an atomic absorption spectrophotometer. The results are shown in ESI Table S3.† The pH adjustment of the wastewater was made by the appropriate addition of 0.1 N HCl. The BDST laboratory-scale column parameters were used for prediction of the service time of the scaled-up column. The values obtained at a given ?ow rate (Q) and initial feed concentration (C0) from laboratory-scale tests were used to calculate the BDST column parameters without further experi- mental determination, according to the relationship proposed by Cooney:33 new slope ¼ old slope QQnoeldw (19) Eqn (19) was used to assess the change in dynamic adsorp- tion capacity with ?ow rate. The intercept of the BDST equation related to adsorption rate constant remained unchanged with ?ow rate, and the new intercept value was thus equal to the old one. On the other hand, the slope and y-intercept of the BDST equation were both changed when the initial feed concentration was changed, and the new values can be calculated as follows: new slope ¼ old slope C0;old C0;new (20) new intercept ¼ old intercept CC00;;noeldw ln½ðC0;new CbÞ 1Š ! ln½ðC0;old C b Þ 1 Š (21) ESI Fig. S5a† shows the breakthrough curves for the indi- vidual heavy metals present in actual wastewater a?er bio- sorption through a 10 cm bed.

43**It can be seen that the breakthrough curves**

44**for the** biosorption **of** Cu **(II), Cd(II) and** Pb **(II)** ions each evolved **in**

a similar manner, resembling the typical S-shape, while deformed breakthrough curves were observed

45**for Cr(VI),** Fe **and Ni(II) ions. The**

deformed break- through curves for

45**Cr(VI),** Fe **and Ni(II) ions** might have been **the** result **of the**

slow adsorption kinetics of these metal ions due to competition from other metal ions possessing greater speci?c binding affinity for certain surfaces. The biosorbent bed also exhibited a lower adsorption capacity for Cd(II) (6.84 10 4

6**mmol g 1) and** Pb **(II)** (9.64 10 **mmol g 1)**

in the case of actual wastewater, compared to 4 that in single and binary synthetic effluents. The loss of

31**adsorption capacity** may **be attributed to the** presence **of** multi- **metal** ions **in the**

actual wastewater. ESI Fig. S5b† shows the percentage removal of each heavy metal, and it is clear that more than 50% of the total

24**Cd(II) and Pb(II)** ions **in the**

real wastewater can still be removed using an appropriate amount of packed biosorbent. The plots of the bed service time at breakthrough, obtained from experimental measurements and prediction by eqn (20) and (21)

51**for Cd(II) and Pb(II)** ions, **are**

presented in ESI Fig. S5c.† For other heavy metals the ?gures are not presented, due to the unavailability of column data from laboratory-scale experi- ments. In Fig. S5c† it can be seen that for a 10 cm bed height, the predicted 1% breakthrough service time for Cd(II) and Pb(II) ions was 30 and 37 min, respectively. On the other hand, the predicted values are quite different from the experimental results, in which the 1% breakthrough service time was 18

44**min for Cd(II) and** 28 **min for** Pb **(II).**

This might suggest that the application of the BDST relationship proposed by Cooney for the purpose of column scale-up was limited to an adsorption system under comparable circumstances. Since real electro- plating wastewater was used in the scale-up experiments, whereas synthetic

24**aqueous solutions of Cd(II) and Pb(II) ions**

were used in the laboratory-scale tests, it is reasonable to expect some deviation between experimental and predicted break- through service time for such adsorption systems with different characteristics. 4. Conclusions The use of a rice straw-packed column has demonstrated potential for removing toxic Cd

21**(II) and Pb(II)** ions **from single and binary** aqueous **solutions. The**

breakthrough and satura- tion of the column is highly dependent on the ?ow rate and bed height. Increased service time of the column can be achieved by the use of greater bed height and a lower effluent ?ow rate. The

46**Yoon-Nelson and dose-response models were** successfully **applied to**

describe the breakthrough curves for single metal systems obtained under varying bed heights and ?ow rates. Both empirical models provided a satisfactory correlation of experimental column data with the coefficient of determination (R2) and theoretical justi?cation of the model parameters. The binary breakthrough curves for binary metal system were reasonably well ?tted by use of the modi?ed Thomas model. Analysis of the binary breakthrough curves revealed that the extent of adsorption competition between the adsorbed solutes was not signi?cantly affected by variations in ?ow rate and bed height. The packed biomass showed good reusability during multiple sorption–regeneration cycles without substantial loss of metal ion sorption capacity. Investigation of the adsorption performance on actual electroplating wastewater containing multiple metal ions demonstrated that the packed bed proce- dure can be applied in a highly effective manner, provided the pH of the wastewater is kept between 5.5 and 6. Spent rice straw can be considered a cheap and renewable biosorbent material

52**for the** effective **removal of** a number **of metal ions in**

large-scale wastewater treatment. Acknowledgements A grant co-?nanced by the International Foundation for Science (IFS), Stockholm, Sweden and the Organization for the Prohi- bition of Chemical Weapons (OPCW) to Felycia Edi Soetaredjo, is gratefully acknowledged. We are also grateful to the National Taiwan University of Science and Technology (NTUST) for providing SEM and EDX facilities. References 1 V. K. Gupta and I. Ali, Sep. Purif. Technol., 2000, 18, 131–140. 2 ATSDR, Priority List of Hazardous Substances, http:// www.atsdr.cdc.gov/SPL/accessed 25 October, 2012. 3 E. Pehlivan, T. Altun and S. Parlayici, Food Chem., 2012, 135, 2229–2234. 4 I. Larraza, M. Lopez-Gonzalez, T. Corrales and G. Marcelo, J. Colloid Interface Sci., 2012, 385, 24–33. 5 J. Huang, M. Ye, Y. Qu, L. Chu, R. Chen, Q. He and D. Xu, J. Colloid Interface Sci., 2012, 385, 137–146. 6 M. Irani, M. Amjadi and M. A. Mousavian, Chem. Eng. J., 2011, 178, 317–323. 7 T. S. Anirudhan and S. S. Sreekumari, J. Environ. Sci., 2011, 23, 1989–1998. 8 L. Fan, C. Luo, Z. Lv, F. Lu and H. Qiu, Colloids Surf., B, 2011, 88, 574–581. 9 S. Chowdhury and P. D. Saha, Colloids Surf., B, 2011, 88, 697– 705. 10 X. Zhang, H. Su, T. Tan and G. Xiao, J. Hazard. Mater., 2011, 193, 1–9. 11 Y. Tian, M. Wu, X. Lin, P. Huang and Y. Huang, J. Hazard. Mater., 2011, 193, 10–16. 12 L. Huang, C. Xiao and B. Chen, J. Hazard. Mater., 2011, 192, 832–836. 13 E. S. Abdel-Halim and S. S. Al-Deyab, Carbohydr. Polym., 2012, 87, 1863–1868. 14 X. Chen, K. F. Lam, S. F. Mak and K. L. Yeung, J. Hazard. Mater., 2011, 186, 902–910. 15 T. Y. Kim, S. K. Park, S. Y. Cho, H. B. Kim, Y. Kang, S. D. Kim and S. J. Kim, Korean J. Chem. Eng., 2005, 22, 91–98. 16 V. K. C. Lee, J. F. Porter and G. McKay, Ind. Eng. Chem. Res., 2000, 39, 2427–2433. 17 H. D. Doan, A. Lohi, V. B. H. Dang and T. Dang-Vu, Process Saf. Environ. Prot., 2008, 86, 259–267. 18 I. A. Aguayo-Villarreal, A. Bonilla-Petriciolet, V. Hernandez- Montoya, M. A. Montes-Moran and H. E. Reynel-Avila, Chem. Eng. J., 2011, 167, 67–76. 19 V. J. P. Vilar, C. M. S. Botelho and R. A. R. Boaventura, Adsorption, 2007, 13, 587–601. 20 S. Mohan and G. G. Sreelakshmi, J. Hazard. Mater., 2008, 153, 75–82. 21 X. Luo, Z. Deng, X. Lin and C. Zhang, J. Hazard. Mater., 2011, 187, 182–189. 22 D. C. K. Ko, J. F. Porter and G. McKay, Chem. Eng. Sci., 2005, 60, 5472–5479. 23 C. W. Cheung, C. K. Chan, J. F. Porter and G. McKay, Environ. Sci. Technol., 2001, 35, 1511–1522. 24 B. Chen, C. W. Hui and G. McKay, Water Res., 2001, 35, 3345– 3356. 25 P. A. Kumar and S. Chakraborty, J. Hazard. Mater., 2009, 162, 1086–1098. 26 D. K. C. Ko, J. F. Porter and G. McKay, Water Res., 2001, 35, 3876–3886. 27 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part B: Applications in Coordination, Organometallic, and Bioorganic Chemistry, Wiley Interscience, New York, 6th edn, 2008. 28 H. C. Thomas, J. Am. Chem. Soc., 1944, 66, 1664–1666. 29 Y. H. Yoon and J. H. Nelson, Am. Ind. Hyg. Assoc. J., 1984, 45, 509–516. 30 G. S. Bohart and E. Q. Adams, J. Am. Chem. Soc., 1920, 42, 523–544. 31 R. A. Hutchins, Chem. Eng. (N.Y.), 1973, 80, 133–138. 32 G. Yan, T. Viraraghavan and M. Chen, Adsorpt. Sci. Technol., 2001, 19, 25–43. 33 D. O. Cooney, Adsorption Design for Wastewater Treatment, CRC Press, Boca Raton, 1998. 34 H. Muhamad, H. Doan and A. Lohi, Chem. Eng. J., 2010, 158, 369–377. 35 K. Vijayaraghavan, J. Jegan, K. Palanivelu and M. Velan, Chemosphere, 2005, 60, 419–426. 36 G. Yan and T. Viraraghavan, Bioresour. Technol., 2001, 78, 243–249. 37 V. Sarin, T. S. Singh and K. K. Pant, Bioresour. Technol., 2006, 97, 1986–1993. 38 J. Cruz-Olivares, C. Perez-Alonso, C. Barrera-Diaz, F. Urena- Nunez, M. C. Chaparro-Mercado and B. Bilyeu, Chem. Eng. J., 2013, 228, 21–27. 39 M. Jain, V. K. Garg and K. Kadirvelu, Bioresour. Technol., 2013, 129, 242–248. 40 Z. Zulfadhly, M. D. Mashitah and S. Bhatia, Environ. Pollut., 2001, 112, 463–470. 41 R. Vimala, D. Charumathi and N. Das, Desalination, 2011, 275, 291–296. 42 A. Singh, D. Kumar and J. P. Gaur, Water Res., 2012, 46, 779– 788. 43 Y. Long, D. Lei, J. Ni, Z. Ren, C. Chen and H. Xu, Bioresour. Technol., 2014, 152, 457–463. 44 A. S. A. Aziz, L. A. Manaf, H. C. Man and N. S. Kumar, Environ. Sci. Pollut. Res., 2014, 21, 7996–8005. 45 R. G. Pearson, J. Am. Chem. Soc., 1963, 85, 3533–3539. 46 I. A. H. Schneider, J. Rubio and R. W. Smith, Int. J. Miner. Process., 2001, 62, 111–120. 47 B. Volesky, J. Weber and J. M. Park, Water Res., 2003, 37, 297– 306. 48 B. Sljukic, C. E. Banks, A. Crossley and R. G. Compton, Anal. Chim. Acta, 2007, 587, 240–246. 49 K. Otto, C. Lehman, L. Bartosiewicz and M. Shelef, Carbon, 1982, 20, 243–251. 50 M. R. Yu, Y. Y. Chang and J. K. Yang, Environ. Technol., 2012, 33, 1553–1559.

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